Plasmonic modes of gold nano-particle arrays on thin gold films *

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Abstract

Regular arrays of metal nanoparticles on metal films have tuneable optical resonances that can be applied for surface enhanced Raman scattering or biosensing. With the aim of developing more surface selective geometries we investigate regular gold nanoparticle arrays on 25nm thick gold films, which allow to excite asymmetric surface plasmon modes featuring a much better field confinement compared to the symmetric modes used in conventional surface plasmon resonance setups. By optical extinction spectroscopy we identify the plasmonic modes sustained by our structures. Furthermore, the role of thermal treatment of the metal structures is investigated, revealing the role of modifications in the crystalline structure of gold on the optical properties.

1   Introduction

Due to their spatially confined electron system, metal nanoparticles exhibit collective electronic modes known as localized surface plasmons (LSP) [1].

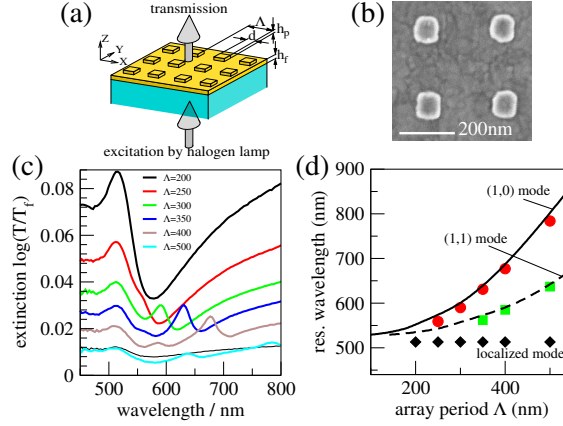[†]e-mail: andreas.hohenau@uni-graz.at

Figure 1: (a) Sketch of the sample and measurement geometries. The samples are illuminated from the glass-substrate side, the transmitted light is collected by a 2.5x, 0.075 numerical aperture objective and analyzed by a spectrometer; (b) Exemplary SEM image; (c) Extinction spectra of particle arrays with varying array periods. The reference for calculating the extinction is taken on the gold film outside the arrays. The thin line depicts the extinction spectrum of a sample with random particle distribution (see text); (d) Resonance wavelengths of the extinction peaks vs. array period: experimental values from (c) (symbols) and calculated values (lines) of different grating orders.

These modes usually occur in the visible spectral range and, if excited resonantly, give rise to spatially highly confined (at the nm scale) optical field enhancement, responsible for surface enhanced Raman scattering (SERS) [2] or surface enhanced fluorescence [3] effects. Optical field enhancement and related surface enhanced effects can be further intensified by electromagnetic interaction between adjacent nanoparticles [2]. In case of particle ensembles on top of a metal surface, their mutual electromagnetic interaction is partly mediated by surface surface plasmon polaritons (SPP) [4]. This interaction was shown to increase SERS efficiency [5], however, a definite assignment of the observed optical extinction peaks to distinct LSP/SPP modes is still missing.

In this work, we investigate the optical modes of regular arrays of gold nanoparticles fabricated by standard electron beam lithography [6] directly

on top of a 25 nm thick gold film (Fig. 1), with array periods of $200 - 500$ nm. The samples are investigated by scanning electron microscopy (SEM) and optical extinction spectroscopy. The investigation of similar systems was reported recently [7, 8], however for different parameter regimes giving rise to different optical modes than those investigated in the following. A systematic variation of the array periods allows us to identify the observed extinction peaks. Furthermore, we assess the potential of such geometries for refractive index sensing.

2 Extinction spectra and peak assignment

Fig. 1(c) depicts the measured extinction spectra of arrays of square gold nanoparticles [Fig. 1(a,b)] with side length $d \sim 100$ nm, height $h_p = 30$ nm and array periods $\Lambda = 200 - 500$ nm on a $h_f = 25$ nm thick gold film. The overall size of the arrays is 100×100 μm. For all array periods we observe one extinction peak at ~ 520 nm and, additionally, a second peak which shifts to larger wavelength for larger array periods Λ. Additionally to these peaks, the extinction spectra show a rise towards longer wavelength. One can assume that the shifting peaks are related to some coupling phenomenon between the particles, while the period independent peak at ~ 520 nm can be assigned to the excitation of a resonance localized to the single particles.

The spectral position of the peaks in the measured spectra [Fig. 1(c)] are plotted in Fig. 1(d) as a function of the array period (symbols). In addition, we plot the calculated grating coupling resonances to antisymmetric SPP modes ('a-modes', defined by the symmetry of the tangential magnetic field with respect to the gold-film plane; the field maximum is at the gold-glass interface) in different grating orders (lines). Due to too small array periods, symmetric SPP modes cannot be excited. The grating coupling resonances were calculated by finding the spectral minima of the denominator of the Fresnel coefficient [9] of an unstructured gold film between glass and air. For the calculation the exciting light wave was assumed to be laterally modulated with a periodicity equal to the array period Λ. We used the actual gold film thickness (25 nm), the optical constants of gold from Ref. [10] and a refractive index of $n = 1.46$ for the quartzglass substrate.

As we find excellent agreement between experimental and calculated data we conclude that grating coupling to a-mode SPPs is indeed observed. The period independent peak at ~ 520 nm can be assigned to a combination
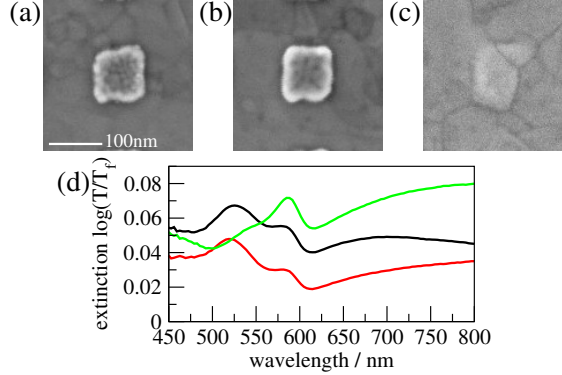
Figure 2: (a) SEM images of a particle after fabrication; (b) after annealing for 30 min at 175°C; (c) after 4h at 200°C; (d) Extinction spectra corresponding to (a) (black line), (b) (red line) and (c) (green line).

of a vertically oriented dipole LSP resonance located at the nanoparticles and scattering to high-energy SPP [11]. To support this interpretation, we fabricated a sample with the same average particle density as the $\Lambda = 500\,$nm array but with randomly distributed particles [thin black line in Fig. 1(c)]. Indeed, in this case only the localized peak and no grating related peaks are observed.

3   Influence of thermal treatment

By comparing the spectra in Fig. 1 with those published by Felidj et al. [5], one observes that the latter show a broad extinction feature at $\sim 650-700$nm instead of the monotonic rise above the grating coupling peaks as observed in Fig. 1(c), although the geometry of the samples was similar. This discrepancy could result from thermal treatment of the gold film. When prepared by vacuum evaporation on glass at room temperature, the gold thin films are built from crystallites about 20 nm large. In the standard lithography process for fabricating samples as used here (and in Ref. [5]) the gold film is covered by an electron resist [6] which has to undergo an annealing procedure (175°C for 8 hours), leading to a recrystallization of the gold [12]. In contrast, the gold nanoparticles on top of the gold film are added later and hence do not undergo thermal treatment. The differences in the surface structure

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of gold film and particles due to the different crystallite size is obvious in the SEM image in Fig. 2(a). The corresponding spectrum [black line in Fig. 2(d)] shows indeed the same broad peak at as observed in Ref. [5]. Further experiments with particles of different shapes and sizes (not shown), revealed no significant change of the spectral position of the grating coupling resonances or the appearance of the broad $\sim 650 - 700$ nm peak.

If we now anneal the whole sample for 30 minutes at 175°C, recrystallization within the particles occurs while their shape is maintained [13] [Fig. 2(b)]. The spectra then show only a monotonic increase of the extinction towards the red spectral range [red line in Fig. 2(d) and spectra in Fig 1]. By further annealing (4h at 200°C), the particles loose their shape and melt into the crystal grains of the substrate [Fig.(2(c)]. In the extinction spectrum, this leads to a disappearance of the localized peak at ~ 520 nm and an increase of the grating coupling peaks [green line in Fig. 2(d)]. We assign the observed differences upon thermal treatment to changes in the particle's dielectric function and shape, in accordance with the finding reported in Ref. [13].

4 Influence of superstratum: potential for sensing applications

Although featuring a field maximum at the gold-glass interface, the a-mode SPP is of considerable strength at the gold-superstrate interface for thin gold films (below ~ 40 nm). Importantly, the a-mode is bound strongly to the interface, giving superior surface selectivity as compared to the conventional surface plasmon resonance (SPR [4]) scheme, making it potentially attractive for refractive index (RI) sensing.

We illustrate this in Fig. 3 by qualitatively comparing the shift of the calculated resonance positions of our arrays with that of the SPR angle. The investigated system consists of a standard glass substrate ($n = 1.52$), a 10 nm (25 nm) thick Au film, an adlayer of varying thickness ($n = 1.4$) and water ($n = 1.33$) as the superstrate. While the slope of the spectral resonance shift of our grating coupling resonance of the 10 nm (25 nm) film is about a factor 4 (8) smaller than for the SPR resonance (thin black line in Fig. 3), the sensing depth (defined as 63% of the maximum peak shift) is ~ 100 nm for the SPR scheme but only ~ 13 nm (~ 26 nm) for the grating coupling
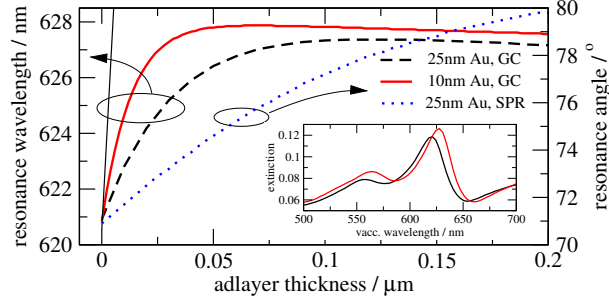
Figure 3: Calculated comparison of the resonance shift for a-mode grating coupling (GC) and SPR. The array periods are chosen as $\Lambda = 151$ nm ($\Lambda = 285$ nm) for the 10 nm (25 nm) film to get a resonance at 620 nm. The thin black line shows the resonance wavelength of the SPR at a constant angle of incidence of $71.8°$. The inset depicts the measured extinction spectra of an array with $\Lambda = 350nm$ nm and $h_f = 25$ nm in air (black) and covered with 10 nm thick SiO_2 adlayer (red).

scheme, i.e., clearly less susceptible to bulk RI changes.

As a proof of principle, we experimentally measured the resonance shift of one of our arrays (after annealing for 4h at $200°$ C) when adding a 10 nm thick SiO_2 on the array-air side. For the array with $\Lambda = 350$ nm we observe a resonance shift of 9 nm of the (1,0) grating peak (inset of Fig. 3). The estimated sensitivity of our current setup is ~ 1 nm SiO_2 in air.

5   Conclusion

We demonstrated that the extinction spectra of regular arrays of gold nanoparticles on 25 nm thick gold films on glass substrate are governed by extinction peaks related to grating coupling to a-mode SPP with a field maximum at the glass-gold interface, and by a resonance localized to the single particles at ~ 520 nm. By annealing of the array the particles fuse with the crystal structure of the substrate, the localized resonance disappears and the grating coupling is enhanced. Such a geometry was used to demonstrate the feasibility of sensing a thin dielectric layer on top of the array by monitoring the resonance wavelength of the grating coupling peaks. The sensitivity is less than for a usual SPR sensor, the surface selectivity is however increased

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by a factor of 4-8 due to the better spatial confinement of the SPP near fields. As an additional advantage we note that due to the grating coupling scheme there is no need for the substrate refractive index to be larger than the superstrate index.

Acknowledgement

References

[1] U. Kreibig and M. Vollmer. *Optical Properties of Metal Clusters.* Number 25 in Springer Series in Materials Science. Springer, 1995.

[2] K. Kneipp, M. Moskovits, and H. Kneipp, editors. *Surface-Enhanced Raman Scattering,* volume 103 of Topics in Applied Physics. Springer, Heidelberg, New York, 2006.

[3] M. Moskovits. Surface-enhanced spectroscopy. *Rev. Mod. Phys.,* 57:783, 1985.

[4] H. Raether. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings,* volume 111 of *Springer tracts in modern physics.* Springer Verlag, Berlin Heidelberg, 1988.

[5] N. Félidj, J. Aubard, G. Lévi, J.R. Krenn, M. Salerno, G. Schider, B. Lamprecht, A. Leitner, and F.R. Aussenegg. Enhanced substrate induced coupling in two-dimensional gold nanoparticle arrays. *Phys. Rev. B,* 65:075419, 2002.

[6] M.A. McCord and M.J. Rooks. *Handbook of Microlithography, Micromachining and Microfabrication,* volume 1. SPIE and the Institute of Electrical Engineers, Bellingham, Washington, 1997.

[7] A. Hohenau, J. R. Krenn, J. Beermann, S. I. Bozhevolnyi, S. G. Rodrigo, L. Martin-Moreno, and F. Garcia-Vildal. Spectroscopy and nonlinear microscopy of Au nanoparticle arrays: Experiment and theory. *Phys. Rev. B,* 73:155404, 2006.

[8] J. Cesario, R. Quidant, G. Badenes, and S. Enoch. Electromagnetic coupling between a metal nanoparticle grating and a metallic surface. *Opt. Lett.*, 30:3404, 2005.

[9] J. J. Burke, G. I. Stegmann, and T. Tamir. Surface-polariton like waves guided by thin, lossy metal films. *Phys. Rev. B*, 33(8):5186, April 1986.

[10] P.B. Johnson and R.W. Christy. Optical constants of the noble metals. *Phys. Rev. B*, 6(12):4370, dec 1972.

[11] W. R. Holland and D. G. Hall. Frequency shifts of an electric-dipole resonance near a conducting surface. *Phys. Rev. Lett.*, 52:1041–1044, 1984.

[12] D. E. Aspens, E. Kinsbron, and D.D. Bacon. Optical properties of Au: Sample effects. *Phys. Rev. B.*, 21(8):3290, 1980.

[13] K.-P. Chen, V. P. Drachev, J. D. Borneman, A. V. Kildishev, and V. M. Shalaev. Drude relaxation rate in grained gold nanoantennas. *Nano Letters*, (10):916, 2009.